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of HMX Plastic-Bonded Explosives

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Pilot-Scale Pressurized Base Hydrolysis of HMX Plastic-Bonded Explosives

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Abstract

A pilot-scale, pressurized, base hydrolysis reactor has been designed and its construction is nearly completed. Up to 120 L of 1-6 M NaOH aqueous solutions will convert as much as 25 kg of consolidated, explosive pieces to non-energetic compounds. Temperatures approaching 155°C in the pressurized unit will reduce reaction times significantly for the destruction of plastic-bonded explosives compared to previous atmospheric-pressure reactors. The hydrolysis effluent is then pumped into a holding tank where it is fed into a hydrothermal oxidation reactor for complete destruction to non-hazardous products. The hydrothermal unit operates at 480°C and 100 MPa and hydrogen peroxide fed into the reactor at two points will ensure complete destruction of all organic species and nitrogen-containing salts. The entire system is comprised of eight major components and is assembled on five separate and transportable skids. Following construction and preliminary testing at Los Alamos National Laboratory, the unit will be shipped to the Pantex Plant where it will be used for continuous demilitarization activities.

Introduction

Disposal of solid energetic materials through economical and environmentally safe means is now sought after to replace many of the current open burning/open detonation (OB/OD) operations. In an effort to develop such technologies, Los Alamos National Laboratory (LANL)[1-4] and others[5-9] have shown that high explosive solids react to form non-energetic, water-soluble products when submerged in caustic solutions. This process is known as base or alkaline hydrolysis. Although no longer explosive, the base hydrolysis effluent must be treated to mineralize organic carbon and convert aqueous nitrogen salts to benign gases. For this reason, LANL has combined base hydrolysis with hydrothermal oxidation (also known as supercritical water oxidation) to transform solid, high explosives pieces into non-hazardous compounds.

Previously, a pilot-scale, base hydrolysis reactor was designed and constructed to treat up to 20 kg of plastic-bonded explosive in a single batch operation. Tests carried out in 1.0-1.5 M NaOH at 90°C and atmospheric pressure resulted in up to 20 hours to destroy a consolidated charge of PBX 9404 weighing less than 16 kg . Since much of the DOE high explosive remediation mission is to dispose of large, pressed pieces, reducing the reaction time became an important concern. Bench-scale experiments indicated that destruction rates for consolidated pieces increased by approximately two orders of magnitude when the reaction temperature was increased from 90 to 150°C. Although reaction

rates were not expected to remain as high in larger reactors because larger pieces have smaller surface-area-to-volume ratios, estimates indicated that, at 150°C, destruction rates for PBX 9404 should increase by a factor of 10 compared to those measured at 90°C. Of course, the hydrolysis rate also depends on the explosive and additives. Another common DOE plastic-bonded explosive, PBX 9501, requires even longer reaction times because the Estane 5703 binder (a polyurethane rubber) is insoluble in water and resistant to attack by base. For this reason, much of the recent effort at LANL investigated base hydrolysis at elevated temperatures and therefore at pressures above ambient. The successful design, construction, and demonstration of a pilot-scale, pressurized base hydrolysis reactor is the next step in developing base hydrolysis as a readily applicable remediation technology.

The primary products of base hydrolysis of nitramine and nitroaromatic explosives (including HMX-based plastic-bonded explosives) are soluble organic carbon species and nitrite and nitrate salts. Hydrothermal oxidation effectively treats such compounds with an oxidizer and water at supercritical water conditions so that levels of harmful chemicals are below that suitable for discharge.

System Components

The design of the base hydrolysis/hydrothermal oxidation reactors called for the entire system to be located on five separate and transportable skids. A schematic of the first skid is shown in Figure 1. This skid houses the base hydrolysis reactor, heat exchangers, transfer and re-circulation pumps. The hydrolysis reactor holds up to 120 L of caustic solution, is steam heated, and pressurized with nitrogen gas to operate at up to 155°C and 1500 kPa (200 psi). The base hydrolysis reactor operates in a semi-batch mode. Up to 25 kg of solid explosive is loaded into the reactor before filling with de-ionized water. Inside the reactor, a plastic-coated cradle holds the explosive. Teflon marbles (1/4 in diameter) placed around the explosive help hold the pieces within the cradle. To initiate reaction, NaOH is fed into the reactor and the reactor is steam heated to reaction temperature. The location of the entry and exit points for re-circulating the solution, screening, and baffling generate a horizontal flow across the explosive. The pumps are suitable for transferring solutions that may contain explosive particles. Because the hydrolysis reactions are exothermic, cooling of the hydrolysate may be necessary to avoid runaway reaction. Cooling can be accomplished using another heat exchanger and chilled water.

In the accumulator, gaseous and liquid products are separated as the hydrolysate solution is re-circulated at 150 L/min. The accumulator also acts as a gas reservoir for pressurizing the system with nitrogen before reaction. After destruction, the non-energetic hydrolysate is filtered to trap any unreacted explosive and pumped into a 1900 L, holding tank. The base hydrolysis system has a designed lifetime of five years with continuous use. Figure 2 is a photograph of the first skid and shows the reactor, pumps, accumulator, and heat exchangers for heating and cooling.

Schematics of equipment installed on the second and third skids are shown in Figure 3. The 1900 L, hydrolysate, holding tank is the main object on skid #2. The holding tank is isolated on a separate skid for two reasons. The first reason is its large size. The second reason is to offer the option of conducting the base hydrolysis and hydrothermal oxidation steps at separate locations. Since the effluent from the base hydrolysis reactor is non-energetic, it is possible, after collecting the hydrolysate, to move the holding tank and carry out the hydrothermal oxidation process at a less restrictive location not necessarily designated for explosive handling or processing.
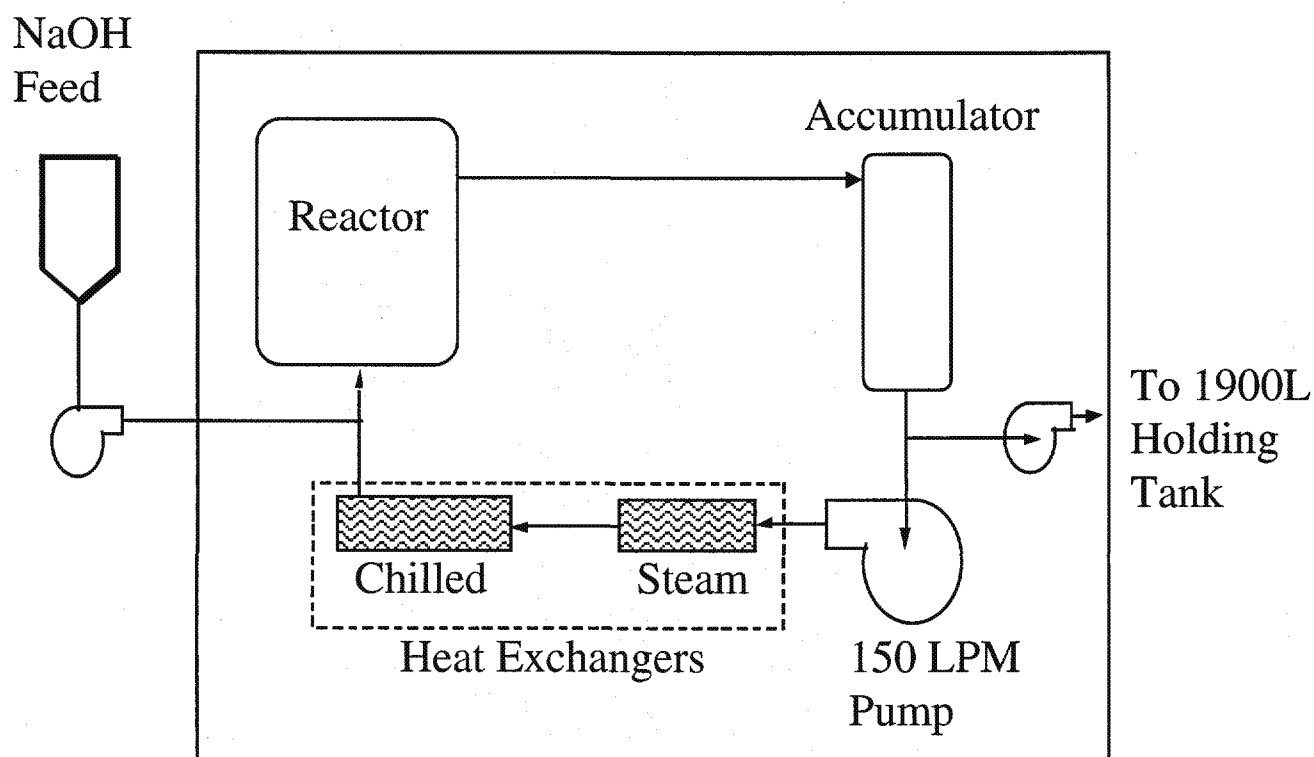
Figure 1. Base Hydrolysis Reactor Skid Schematic.

Also included on skid #2 are de-ionized water containers and a pump to transfer liquid to high-pressure pumps, which feed the hydrothermal oxidation reactor. The de-ionized water is used for the startup and shutdown of the reactor.

Skid #3 contains high-pressure pumps that deliver the hydrolysate to the hydrothermal oxidation reactor at approximately 100 MPa (15,000 psi). The flow generated by these Hydro-Pac pumps is 0.8 L/min. Two other, smaller pumps supply hydrogen peroxide to the hydrothermal oxidation reactor. A 400 L tank containing the 30 wt% hydrogen peroxide solution is also mounted onto skid #3. Hydrogen peroxide was used instead of gaseous oxygen to ensure complete mineralization of organic carbon due to the relative ease of pressurizing and injecting a liquid stream into the reactor compared to a gas. The photograph in Figure 4 shows skid #2 in the background and to the left and skid #3 in the center.

Schematics of the final two skids are shown in Figure 5. Skid #4 holds the hydrothermal oxidation reactor. This unit consists of a 795 ft, Iconel 625 tube wrapped into a 4 ft-diameter coil, which stands 3 ft high. The tubing diameters are 0.188-in ID and 0.375-in OD. The tubular reactor will be wrapped in blanket insulation and housed inside a 1/8-in thick aluminum shell. Heat exchangers at the inlet and outlet and a 37 ft, electrically-heated tube raise the inlet hydrolysate stream to 300 to 600°C (typically ~480°C). At these temperatures and pressure (100 MPa), accumulation of salts inside the tubular reactor is avoided. Conversions of 99.5 to 99.9% of organic carbon and nitrogen to benign products (CO_2, N_2, and N_2O) are expected.
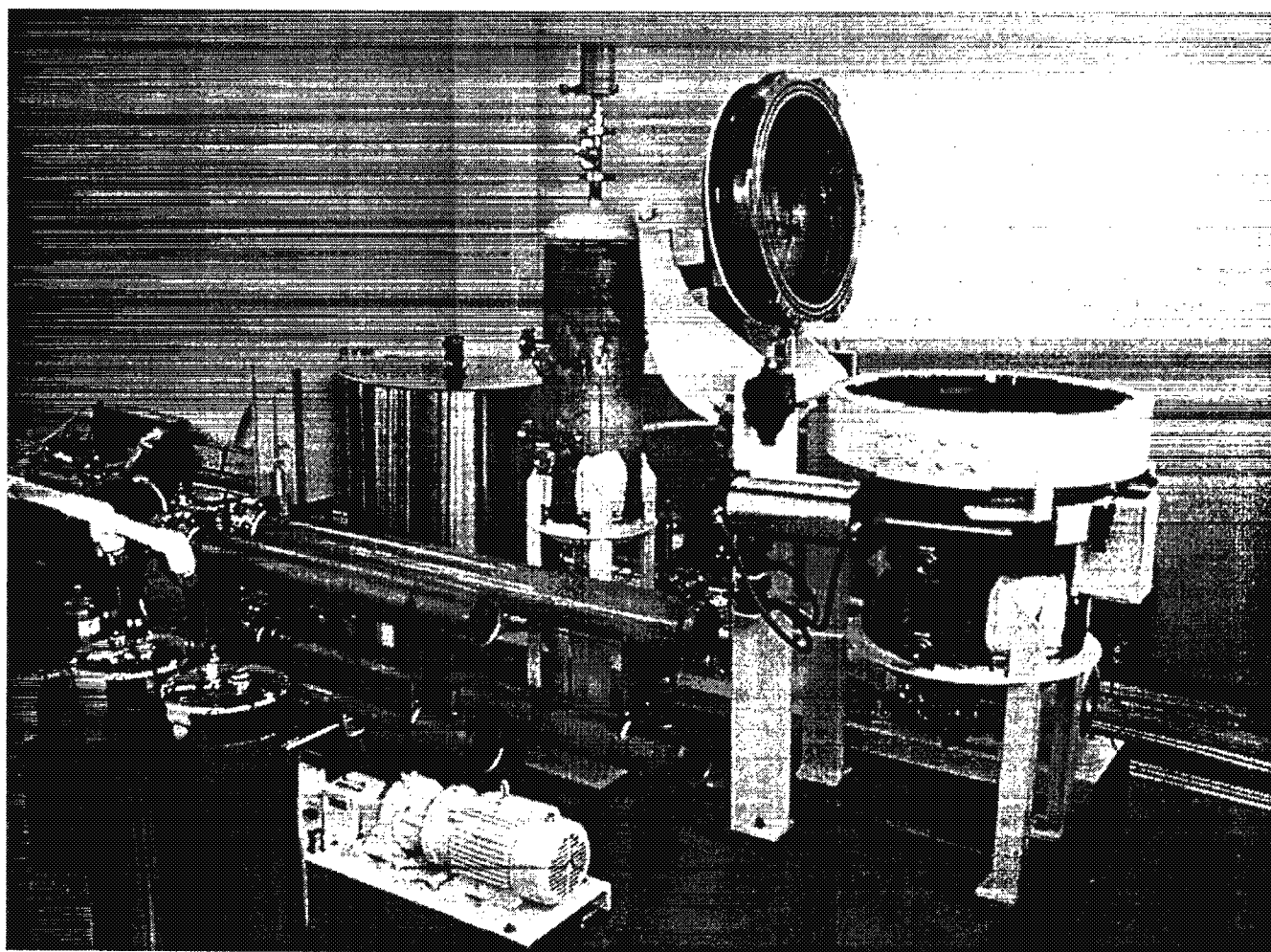
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Figure 2. Base Hydrolysis Reactor Skid Photograph.

Ideally, all nitrates and nitrites should be converted to N_2 gas and all carbon to CO_2 or dissolved HCO_3^-. Unfortunately, the reactions that produce these compounds compete with each other since both are oxidation reactions. One approach to achieve high conversion of nitrogen salts and organic carbon species is to increase the reaction temperature. Increasing the temperature predicates higher reaction pressures to eliminate fouling through Na_2CO_3 precipitation. Another approach is to inject additional oxidant (hydrogen peroxide) into the tubular reactor at positions downstream from the reactor inlet to maintain a more constant oxidant concentration throughout the reactor. The design of the hydrothermal oxidation reactor incorporated both of these approaches. Figure 6 is a photograph of skid #4 and the tubular coil that is the hydrothermal oxidation reactor.

The final skid, skid #5, has a product recovery tank for the outlet stream of the hydrothermal oxidation reactor. In addition, control equipment, which operates equipment on all of the skids resides on skid #5. Controls are based on Allen Bradley software, in which the operator monitors the processes using a personal computer.
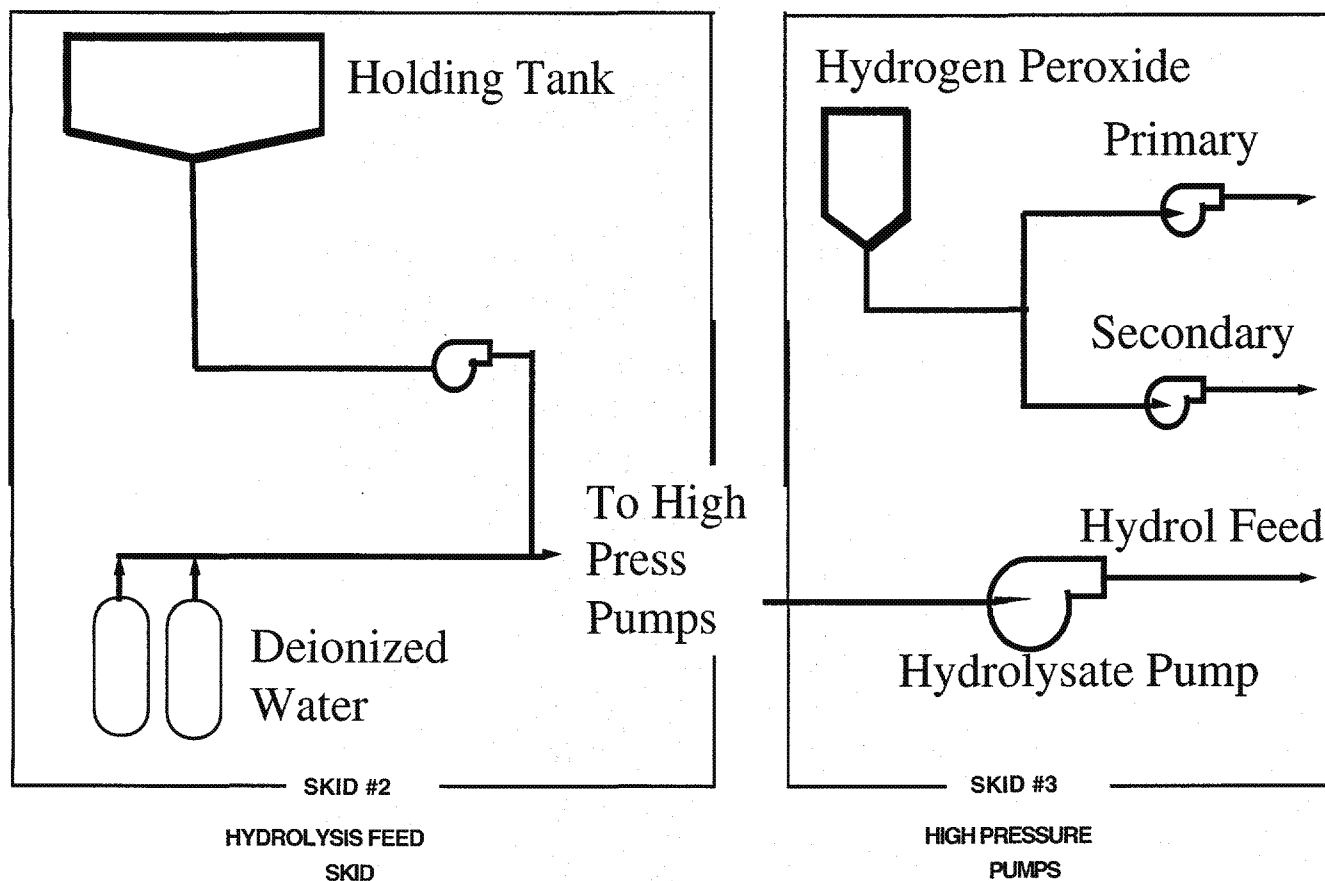
Figure 3. Schematic of Hydrolysate Feed and High Pressure Pump Skids.

In addition to the five skids, three other pieces of equipment are necessary for this system. Factory-built steam generator and cooling tower provide heating and cooling of the base hydrolysis reactor. These units have been purchased and are being wired for instrumentation and plumbed. A power generator is also required, but one will be rented initially for the preliminary test runs.

Operation and Safety

The main safety concern is the operational temperature of the base hydrolysis reactor and the question as to whether or not a runaway reaction causing unacceptable heating and subsequent explosion of the remaining high explosive can occur. The atmospheric-pressure, base hydrolysis reactor previously built at LANL can not undergo excessive temperature rise due to a possible runaway reaction because added energy to the system simply boils off the NaOH solution. However, in a closed and pressurized vessel, this solution may conceivably reach temperatures at which the explosive in the reactor may become unstable and thus unsafe.

Our laboratory work has shown that base hydrolysis at 150°C can be carried out for 400 g of HMX crystals or PBX molding powder and 130 g of a consolidated piece of PBX 9404. We have not carried out pressurized base hydrolysis experiments for larger amounts of explosives in the laboratory. These results do not provide enough evidence that larger pieces can also undergo base hydrolysis at

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150°C safely. For this reason and to determine a maximum safe base hydrolysis temperature for the pilot-scale system, a series of laboratory experiments are being planned and conducted. In these experiments, a hydrolysis reaction is intentionally heated as high as 300°C to observe whether or not the explosive (375 mg) reacts violently and to measure the temperature at which a violent reaction occurs.
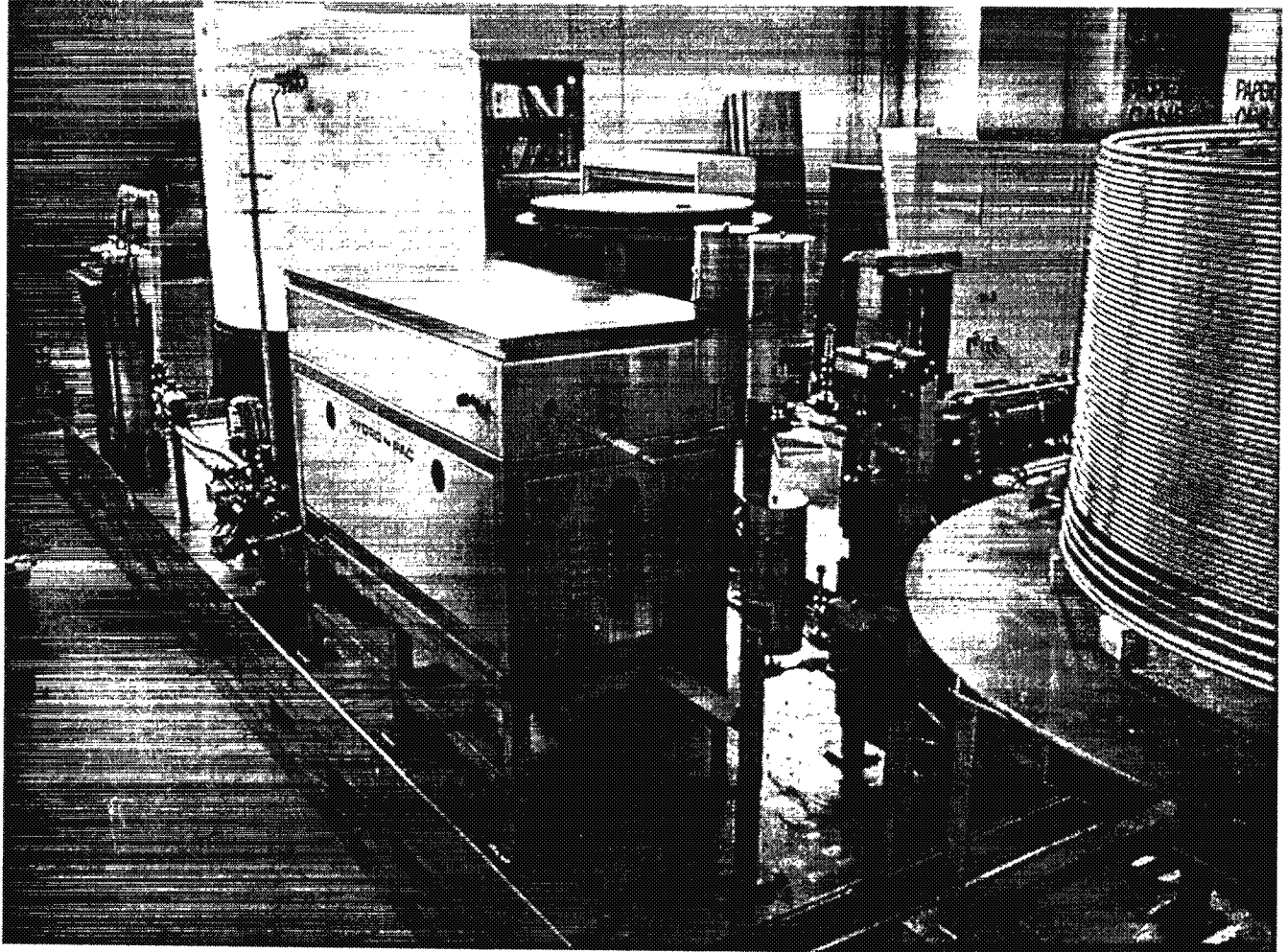

Figure 4. Photograph of Hydrolysate Feed and High Pressure Pump Skids.

Based on the results of these experiments and others planned for a 7-g, scaled-up system, a predictive model will be generated, which will indicate a safe operating temperature for the pilot-scale base hydrolysis reactor. Preliminary results indicate that temperatures above 185°C may be unsafe. Once the operational temperature is determined, test runs of the pilot-scale unit will be carried out remotely at LANL. After shake down of the system and sufficient operation experience, this entire unit will be shipped to the Pantex Plant in Amarillo, TX for use in demilitarization efforts.
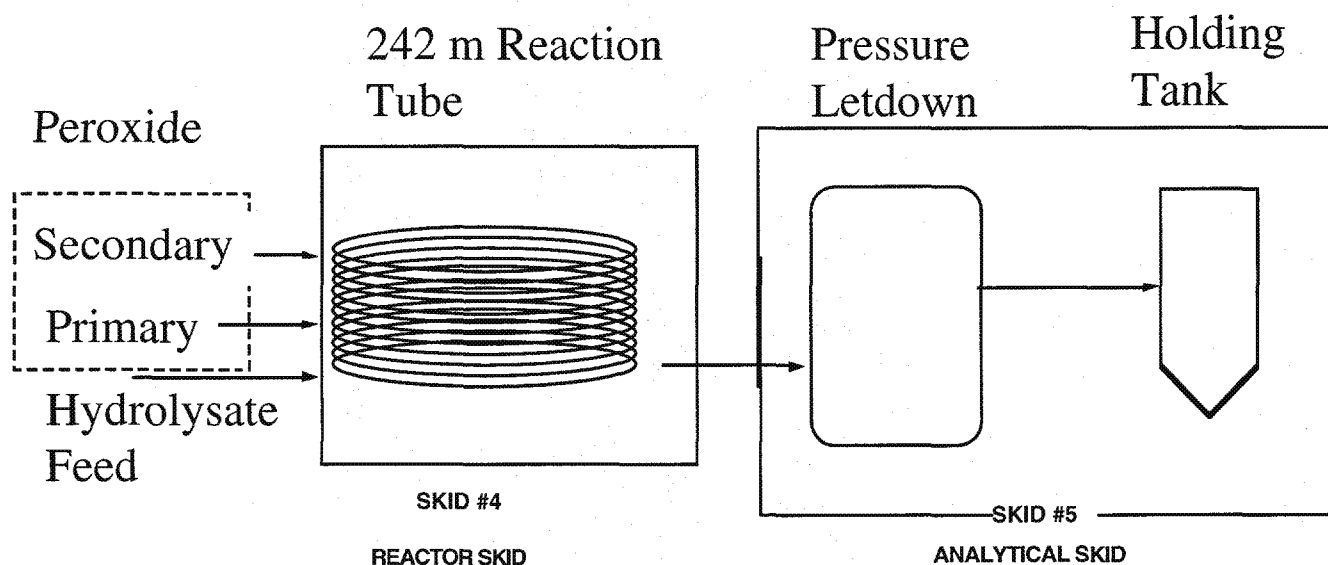
Acknowledgements

Figure 5. Schematic of Hydrothermal Oxidation Reactor and Analytical Skids

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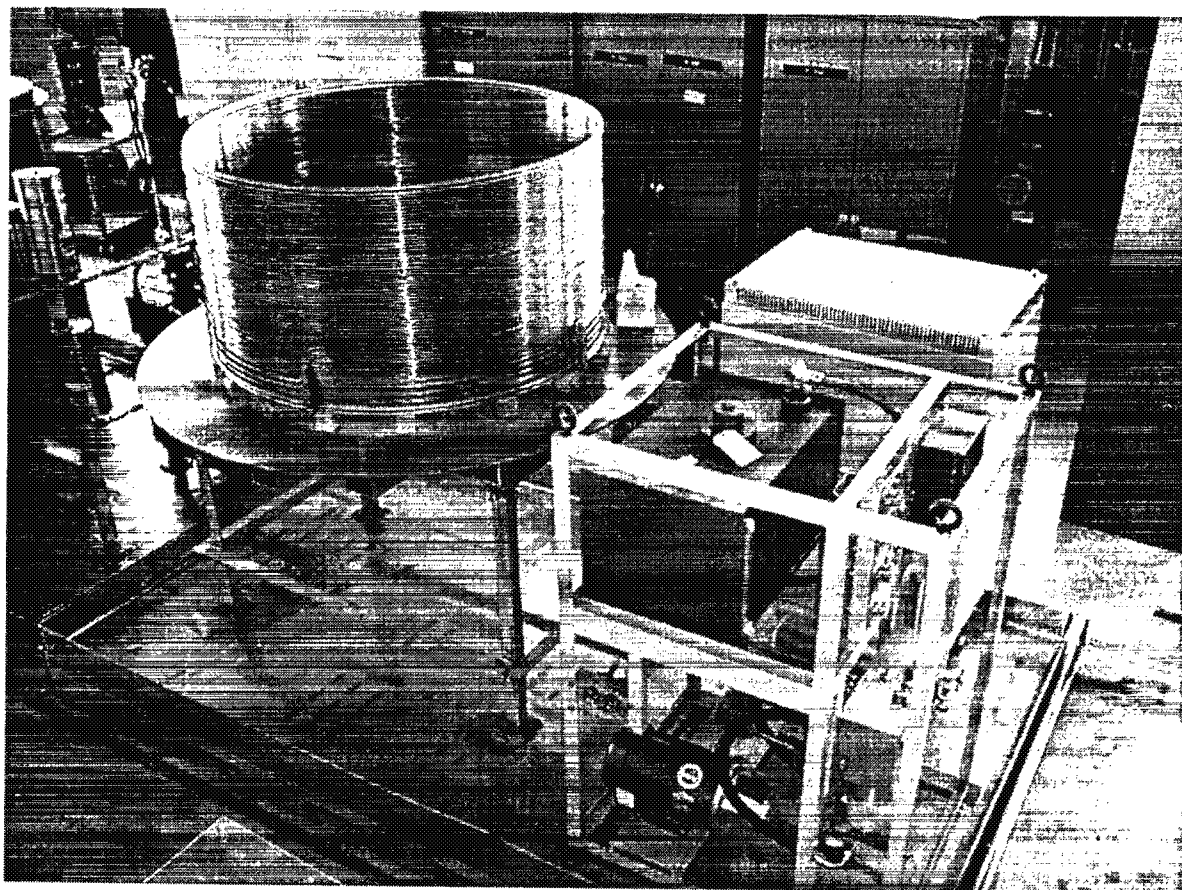
Figure 6. Photograph of Hydrothermal Oxidation Reactor.